(12) UK Patent (19) GB (11) 2 049 952 B

(54) Title of invention

Gas sensor

(51) INT CL³: G01N 27/50

(21) Application No
8015007

(22) Date of filing
6 May 1980

(30) Priority data

(31) 7917237

(32) 17 May 1979

(33) United Kingdom (GB)

(43) Application published
31 Dec 1980

(45) Patent published
30 Mar 1983

(52) Domestic classification
G1N 19F1X 25A1 25C3X 25D2
25E2 BPX
U1S 1484 1451 1459 2159
G1N

(56) Documents cited
None

(58) Field of search
G1N

(73) Proprietors
City Technology Limited
(Great Britain),
The City University,
Northampton Square, London
EC1V 0HB

(72) Inventors
A. D. S. Tantram,
Yat Shein Chan

(74) Agents
Gill Jennings and Every,
53/64 Chancery Lane, London
WC2A 1HN

GB 2 049 952 B

Fig.1.

Fig.2.

13A

15

14A
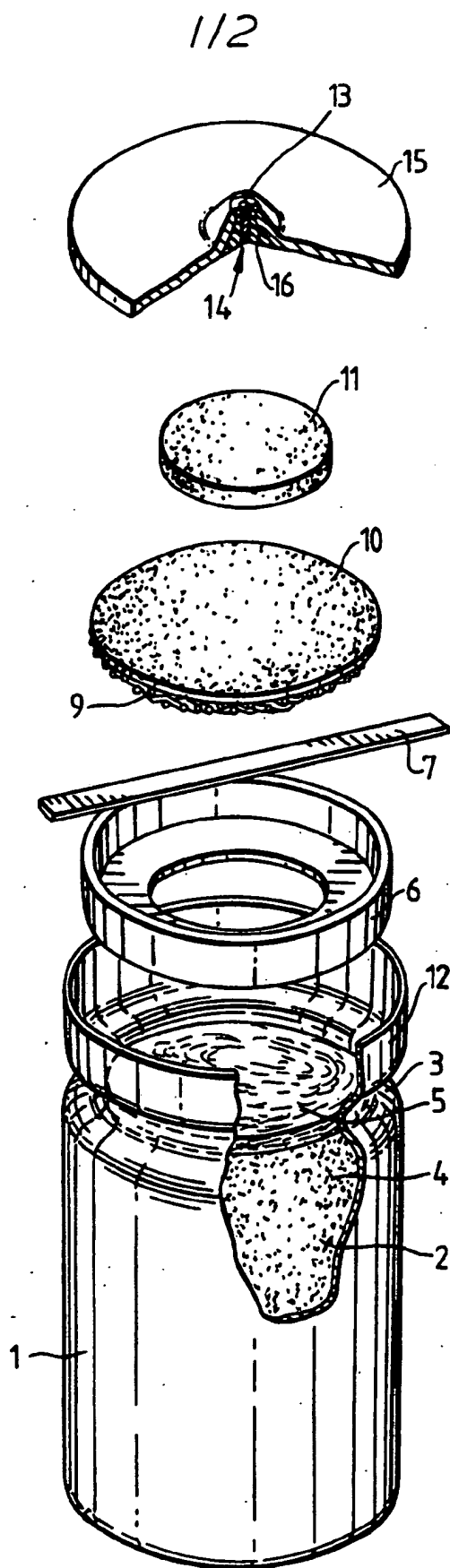
Fig.3.
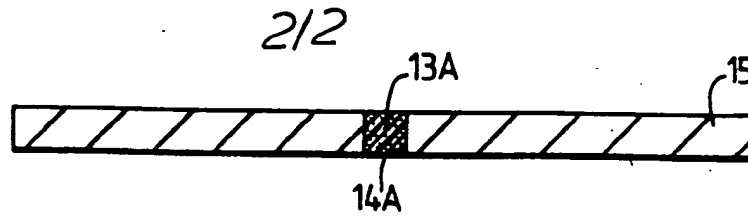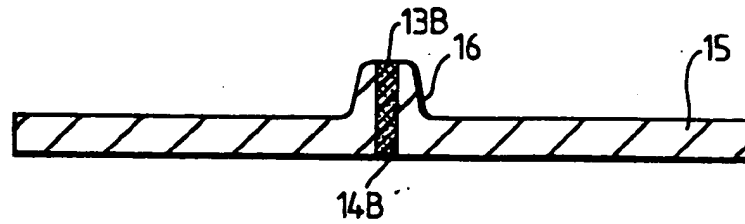
13B 16

15

14B

Fig.4.

21

20

19

18

15

14

Fig.5.
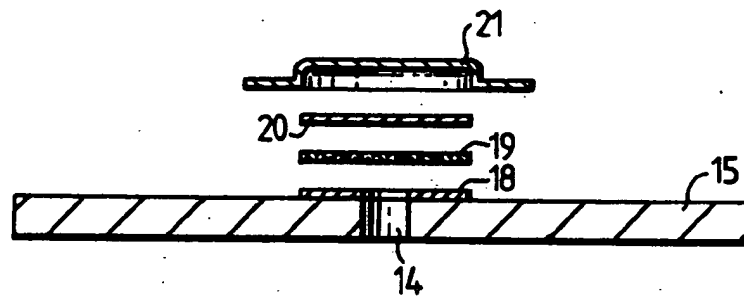
21

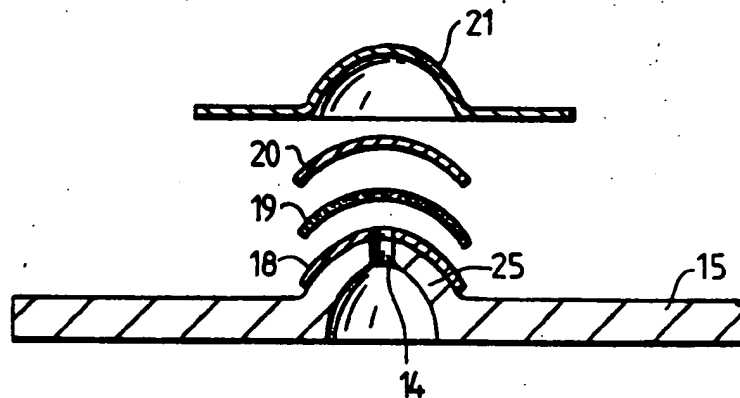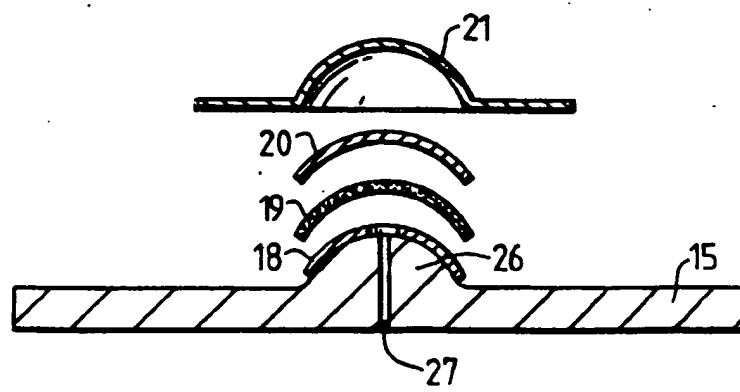20

19

18 25

15

14

Fig.6.

21

20

19

18 26

15

27

SPECIFICATION
Gas sensor

This invention relates to electro-chemical gas
sensors in which the gas or vapour to be sensed is
5 caused to react at one electrode of an electro-
chemical cell, which also includes a counter
electrode and an intervening body of electrolyte, in
such a way that the current through the cell is a
function of the partial pressure of the gas or
10 vapour to be sensed. The principle will be
described in relation to the sensing of oxygen
although it is to be understood that it is applicable
to any gas or vapour which can be electro-
chemically reacted in this way. Gases or vapours
15 such as, for example, oxygen and nitrogen oxides
which are electro-chemically reducible, are sensed
at the cathode, while those which are electro-
chemically oxidisible, such as carbon monoxide,
sulphur dioxide and hydrogen sulphide are sensed
20 at the anode.

In practice oxygen is electro-chemically
reduced at an oxygen cathode, to which the rate of
access of oxygen is restricted, for example by a
diffusion barrier, under conditions such that the
25 electrode is operating in the so-called limiting
current region. The general principles and practical
considerations involved are described in some
detail in U.S. patent no: 4,132,616. In particular,
Figure 1 of the drawings of this earlier
30 specification illustrates the limiting current
principle.

There is a continuing demand for reliable and
easy to operate gas sensors. Oxygen sensor, for
example, are required for oxygen deficiency
35 monitoring for safety purposes where personnel
have to work in confined spaces. Here small,
portable, inexpensive, robust and reliable sensors,
which can readily be used by unskilled personnel
and which are substantially unaffected by ambient
40 changes, e.g. temperature, humidity, are most
important. Oxygen measurement is also important
in a wide range of other applications, e.g.
combustion control, process control and other
industrial applications. In some applications it is
45 the partial pressure of oxygen that is the important
parameter, for example for measurement of
breathing gases at pressures appreciably differing
from ambient. In others the concentration, or
percentage oxygen is the more important
50 parameter, for example in process control
applications. In cases where no pressure changes
are encountered, it is not greatly significant
whether the sensor measures partial pressure or
percentag .

55 As explained in the U.S. specification, most of
the known types of gas sensors working on these
general principles achieve the necessary
restriction to the access of gas to th sensing
electrode by the provision of a non-porous solid
60 membran b tween the body of the gas to be
test d and the s nsing lectrode so that the flux of
gas is restrict d by the diffusion rate of gas in soluti n
in the solid membrane. Examples of such solid
membranes that have been used are films of

65 polytetrafluoroethylene, polyethylene and silicone
rubber. An example of a sensor using such a
membrane is that described in S.M.R.E. Digest,
Gas Detection, 1. 1972.

The use of non-porous solid membrane films
70 has the disadvantage that very thin membranes
have to be used to achieve practical current levels
and more importantly that the resulting sensor has
an extremely high temperature co-efficient, which
may be as high as 2% to 3% per degree
75 centigrade. This means that provision must be
made for temperature compensation and this is
difficult to achieve accurately and reliably. This
high temperature co-efficient is a fundamental
consequence of the process of transporting gas in
80 solution through a solid material, being associated
with the high activation energy required for this
purpose.

The U.S. specification referred to above
describes and claims a form of gas sensor which
85 includes a gas phase diffusion barrier (referred to
subsequently as a GP barrier) to provide the
necessary controlled restriction to the access of
gas to the sensing electrode. This barrier may be
in the form of a simple capillary, a porous sheet or
90 a combination of these.

The essential features of a GP diffusion barrier
are:—

(a) that the gas remains in the gas phase during
its diffusion through the barrier (b) that the
95 diffusion resistance is provided by the molecules
of the gases present (hence the term gas phase
diffusion barrier) so that the diffusion mechanism
and hence the laws governing diffusion are
determined by inter-molecular collisions in the gas
100 phase. The capillary or porous sheet serves to
contain this gas phase diffusion barrier and control
and define its geometry.

It will be seen from the description above that
the characteristics of the resulting sensor depend
105 upon the type of diffusion barrier used.

According to the present invention, a sensor
operating on the limiting current principle as
described above, utilises a porous diffusion barrier
to provide the necessary limitation to the rate of
110 diffusion of gas to be sensed, of which
substantially all the active pores are sufficiently
small as to cause diffusion through them to be in
accordance with the Knudsen principle. Diffusion
in accordance with this principle is characterised
115 by the fact that the diffusion mechanism is
effectively determined solely by collisions
between the diffusing molecules and the walls of
the pores and the term "Knudsen diffusion" is
used in this sense throughout the sp cification
120 and claims, refer nc s to a Knudsen diffusion
barrier b ing abbreviated to KD barrier for
convenience.

Details f Knudsen diffusi n have been
described, for example, in "Heat and Mass
125 Transfer in Capillary-Por us Bodies", Lykov. A.V.,
Pergamon, 1966. Th mechanism of this type of
diffusion is radically different from that applying to
the diffusi n barriers already d scribed namely,
the GP barri r, contr lled by inter-molecular

collisions in the gas phase and the solid membrane barrier (SM barrier) controlled by diffusion in solution. Consequently the laws governing diffusion are different and this in turn
5 leads to sensors having significantly different characteristics from GP barrier or SM barrier sensors, and to characteristics which give rise to specific advantages in specific situations.

Thus, for example KD barrier sensors have an
10 intrinsically low negative temperature co-efficient of about −0.17°C per °C in the ambient range (reflecting a $T^{-\frac{1}{2}}$ law resulting from the Knusden diffusion mechanism where T is the absolute temperature), which is sufficiently low for
15 temperature compensation not to be necessary in many applications. This temperature co-efficient is in marked contrast to the high positive co-efficient of SM barrier sensors and also differs from GP barrier sensors in that it is negative rather than posi-
20 tiv . It is also found that sensors according to the present invention respond to partial pressure rather than concentration (% by volume) and that the response to partial pressure is linear over a wide range, thus distinguishing them further from
25 GP barrier sensors.

In the selection of suitable materials for KD barriers, pore size is the primary criterion. As xplained above, the phenomenon of Knudsen diffusion is determined by collisions between the gas
30 molecules and the walls of the pores and thus imposes the requirement that the size of the pores in the KD barrier are sufficiently small that the number of inter-molecular collisions becomes insignificant compared to the number of molecule to
35 wall collisions. As a starting guide it can be said that the pore diameter needs to be less than the mean free path of the gas molecule in question. In the case of oxygen for example, this is about 9.5 × 10^{-6} cm at ambient temperature and pressure. As
40 mentioned previously, it is necessary that substantially all the pores throughout the barrier should be well into the "Knudsen" region to ensure that Knudsen diffusion is the governing mechanism.

Such small pore sizes, and their distribution, are
45 difficult to measure and as a result selection of materials by attempts at direct measurement of pore size is unsatisfactory. Moreover, we have found that manufacturer's specifications as to pore size cannot be taken as a reliable guide in this
50 context. For these reasons, and since it is the diffusion characteristics that are the property most directly pertinent to this invention, materials are best selected by a direct examination of the diffusion characteristics.
55 As described above, a specific characteristic is the low negative temperature co-efficient and it can therefore be deduced that, if the diffusion rate has a negative temperature co-efficient of around −0.17% per °C at ambient temperatures, the
60 material under test should be a satisfactory KD barrier. This th oretical t mperature co-efficient of −0.17% per °C may be modified slightly in practice due to differential thermal expansion effects. A c nvenient way of carrying out such a
65 test is in fact to make up an oxyg n s ns r

incorporating the diffusion barrier and to measure its temperature co-efficient. To carry out such tests the diffusion barrier needs to be suitably mounted and effectively sealed in position. Since
70 it is necessary that Knudsen diffusion should be the controlling gas transport mechanism it is clear that any leakage path, along which Knudsen diffusion would not occur, needs to be avoided. Measurement of the pressure co-efficient will
75 provide a confirmatory test, since the diffusion rate (or signal from the oxygen sensor at a given % oxygen) will be substantially proportional to total pressure for a KD barrier, whereas for a GP barrier, such as described in the U.S. specification, the
80 diffusion rate (or signal from the oxygen sensor at a given % oxygen) is substantially independent of total pressure.

Tests, such as those described above, with a wide range of materials have brought to light a
85 further desirable criterion to ensure that a satisfactory KD barrier is achieved in practice, namely the aspect ratio of the barrier. More specifically if a simple case is considered where the KD barrier is in the form of a cylinder with
90 diffusion occurring along the length of the plug, then the diameter of the barrier plug should be less than twice the length of the plug. It will be appreciated, as will be illustrated later, that the KD barrier can take a variety of different geometric
95 shapes. The criterion illustrated above can be therefore stated in a more general form as follows:—

The ratio

$$\frac{X}{L}$$

100 should be less than 2 where x is the minimum linear dimension across the part of the KD barrier through which diffusion is occurring in the direction of diffusion and L is the mean linear dimension along the overall direction of diffusion.
105 Should the KD barrier effectively comprise a number of individual KD barriers in parallel then the dimension x refers to the individual KD barrier.

It is found that various commercially available
110 porous PTFE tapes, often referred to as "unsintered" tapes, may have sufficiently small pores as to give Knudsen diffusion, but the proporties of such tapes are somewhat erratic and are found to vary from one production batch to
115 another. Accordingly it is necessary t subject any sample of such tape to the previously described test for diffusion. If the result of such a test is unsatisfactory it may b possible to improve th diffusion characteristics. Such tapes ar
120 anisotropic and, in one direction, usually al ng the length of the tape, ar resistant to stretching. In the other direction, i.e. across the width of the tape, they can be readily stretched to several times the original widths. It has been found in a
125 number of cases that this tr atm nt will produce a

material giving Knudsen diffusion, and suitable for a KD barrier, particularly when mounted so that diffusion through the barrier was along the direction of stretching, even when the starting

5 tape was unsuitable, as evidenced by the tests mentioned earlier. If the results are still unsatisfactory, the sample must be rejected.

The following are some exmples of commercially available tapes that have been found

10 to have the required characteristics:

(1) A 0.24 mm thick PTFE tape supplied by W. L. Gore and Associates (UK) Limited, described as clear, unsintered, unstretched tape and having a porosity of about 15%;

15 (2) "Gore-tex" S10633 from the same suppliers;

(3) "Tygaflor" (R.T.M.) R 128 gauge 7T supplied by Tygadure Limited.

In a particular example a tape in accordance with

20 (1) above was stretched laterally to six times its original dimension. The effect of stretching was found slightly to increase the thickness to 0.32 mm, but radically to reduce the longitudinal dimension as the lateral dimension was increased.

25 Using a piece of the resultant membrane having a length in the stretched direction of 3 mm and a width of 1.5 mm as a diffusion barrier in an oxygen sensor, mounted, as described later, and in such a way that the diffusion through the tape was

30 along the direction of stretching, gave a resultant temperature co-efficient of −0.175% per °C when measured over the range 10°C to 40°C.

Other commercially available material from which a membrane yielding Knudsen diffusion

35 may be obtained is a dispersion of PTFE in water such as that manufactured by Imperial Chemical Industries Limited under the name "GP1" and a similar dispersion manufactured by Du Pont de Nemours Inc. The dispersion comprises minute

40 particles of PTFE in suspension and when dried and the dispersing agent removed, yields a pasty mass which may be readily consolidated by the application of pressure. The dispersing agent may be removed, for example by solvent

45 extraction or by heat treatment at around 270°C for about one hour.

The pressure required for consolidation is to some extent dependent on the geometry of the KD barrier being constructed, but may be readily

50 established by experiment. As a guide it has been found that so long as the pressure is above about 1000 psi the resultant compact will normally yield Knudsen diffusion and be suitable for a KD barrier, as indicated by the diffusion/sensor tests already

55 mention d.

By consolidating the material in situ in a suitably sized hole in the sensor top cap, it is caus d to conform with the shape of the hole and thus to prev nt any leakage. In a particular

60 example, a quantity of the pasty material referred to was pressed into a hole of diameter 1.5 mm and length 1.3 mm and was consolidated at a pressure of about 2000 psi. This gav an oxygen sensor having a temperature co-efficient of

65 0.165% per °C, thus demonstrating that the

resultant pores were small enough to produce Knudsen diffusion.

Other constructional features will now be described in more detail with reference to the

70 accompanying drawings, (not to scale), in which:—

Figure 1 is an exploded perspective view of a complete sensor including a top cap fitted with a KD barrier;

75 Figures 2 and 3 are cross sectional views to an enlarged scale of alternative constructions of top cap for substitution in the construction of Figure 1;

Figures 4 and 5 are exploded cross sectional views of further forms of top cap; and

80 Figure 6 is an exploded cross sectional view of a top cap similar to that shown in Figure 5, but including a gas phase barrier in series with the KD barrier.

The basic construction of cell shown in Figure 1

85 is similar to that illustrated in the U.S. patent referred to previously and comprises a metal can 1, for example of nickel plated steel, which contains and electrically contacts a counter-electrode 2 which forms the anode when the

90 device forms an oxygen sensor. The electrode 2 may, for example, be of a lead wool extending up to just below the level of a rill 3. The porous electrode 2 is filled with electrolyte 4, for example sodium hydroxide. A wicking separator 5 which is

95 permeable to electrolyte but is electrically insulating is fitted on top of the electrode 2 and above this is an insulating grommet seal 6. A narrow strip of thin metal foil 7, for example silver, connects a sensing electrode 9 to the outside of a

100 metal top cap 15 when the cell is finally closed. A waterproofing layer 10 of porous PTFE is pressed to the electrode 9 to form a unitary assembly and a porous disc 11, for example of plastic, is fitted immediately beneath the top cap 15 to ensure a

105 good spread of diffusion of gas passing through the top cap 15. The components just described are stacked one on top of the other and the assembly is completed by folding over an upper rim 12 of the can 1 to hold all the components in

110 position.

The top cap 15 shown in Figure 1 constitutes one example of which the remaining Figures show further examples. The top cap 15 has a central opening 14 surrounded by a raised portion of the

115 cap and a KD barrier 13 is fitted in this opening, being sealed in position by melting of a hot melt adhesive or by potting with a resin shown as 16. In this example, the KD barrier 13 is constituted by a piece of stretched PTFE tape as previously

120 described which is mounted so that the diffusion path through th barri r is along th direction f the stretch. In assembly, a l nger than nec ssary l ngth of tape is used so that it can subsequently be trimm d flush at the top and bottom of th top

125 cap 15.

Figures 2 and 3 sh w top caps 15 designed for KD barriers formed of pressed PTFE powder, as previously describ d. In Figure 2 a central opening 14A is formed within the thickness of the cap 15

130 and in Figure 3, a central op ning 14B is formed

within a thickened porti n 16 of the top cap to
give a greater length of barrier. The barrier itself is
shown as 13A and 13B respectively in the two
Figures and in each case, during manufacture, the
5 PTFE powder is extruded into the openings 14A,
14B and then consolidated by pressure, preferably
in a mould incorporating elastic rubber discs
against the top and bottom of the top cap 15, in
order to improve sealing distribution. It is found
10 that excellent sealing results from this method in
which the material is consolidated in situ since it is
caused to conform with the shape of the opening
14A, 14B. However, severe low temperature
cycling can open up channels between the top cap
15 15 and the KD barrier 13A, 13B which are of a
size as to permit non-Knudsen diffusion. This
consequence may be avoided by pre-coating the
opening 14A, 14B with a sealant, for example a
pressure sensitive adhesive, or with a hot melt
20 adhesive. When using the latter material, the top
cap 15 together with the barrier 13A, 13B is
subsequently raised to the adhesive melting point
to effect a stable seal.
The examples shown in the remaining Figures
25 are all intended for use with KD barriers formed of
PTFE tape which may or may not be stretched,
according to the properties of the tape as initially
manufactured. In Figure 4 the top cap is again
shown as 15 and the central opening as 14.
30 Immediately above the top cap 15 is a thin layer
18 of adhesive sealant. This is followed by a piece
of PTFE tape 19 constituting the KD barrier and
above that an adhesive sealing barrier film 20, the
assembly being enclosed by a sealing cap 21
35 which may, for example, be of nickel foil and
which is attached firmly to the top cap 15, for
example by spot welding around its perimeter. The
sealing film 20 may take the form of a non-porous
adhesive coated plastic tape or may be a thin layer
40 on the underside of the cap 21. The sealing cap 21
contains a number of gas access holes drilled
annularly at a diameter just greater than that of
the KD barrier 19 to allow gas access to the
perimeter of the barrier. Diffusion then occurs
45 radially inwardly so that for the purposes of
determining the aspect ratio of the barrier, the
mean linear dimension along the overall direction
of diffusion is equal to the radial dimension of the
barrier 19 while the minimum linear dimension
50 across the part of the barrier through which
diffusion occurs is the thickness of the barrier.
The construction of Figure 5 includes the same
components as that of Figure 4 and these are
therefore identified by the same reference
55 numerals. The construction is modified by the
provision of a domed portion 25 surrounding th
opening 14 in th centre of the top plate 15. As a
consequenc , the components 18, 19, 20 and 21
are all similarly domed to fit the portion 25 and it
60 is found that this facilitat s sealing.
The construction of Figure 6 represents a
further modification in that the central portion of
the top cap 15 is thick n d as shown at 26
instead of merely being domed. The components
65 18, 19, 20 and 21 are all the same as in Figure 5,

but the central opening shown as 27 is
appreciably longer, owing to the thickening 26
and is of capillary size so as to define a GP barrier
in series with the KD barrier constituted by the
70 PTFE tape 19. The advantage of such a
construction is that the small negative co-efficient
of the KD barrier is counter-acted by the
correspondingly small but positive co-efficient of
the GP barrier. By suitable selection of the
75 characteristics of the two barriers, a temperature
co-efficient of substantially zero may be obtained
which is advantageous in many applications.
Other operating characteristics of a sensor using a
combination of barriers of the two types are found
80 to be intermediate between the characteristics of
KD and GP barrier sensors.
The use of a KD barrier, in particular when it is
in the form of consolidated PTFE powder, as
illustrated in Figures 2 and 3, enables the overall
85 construction to be simplified in a manner not
illustrated in the drawings. Since such a KD barrier
is hydrophobic and resistant to electrolyte
penetration, the waterproofing layer 10 illustrated
in Figure 1 and also the disc 11 may be omitted
90 and the electrode 9 may be mounted directly
against the KD barrier. It has also been found that
if the electrode material, that is to say catalyst
plus PTFE, is pressed directly onto the underside
of the top cap 15, the top cap having been first
95 thinly coated with adhesive if necessary, there is a
sufficient electrical connection between the
electrode and the top cap to avoid the need for
the contact strip 7.
The level of the signal required from the sensor
100 depends to some extent on the particular
application and also on the active life required in
relation to the available anode capacity. It will be
seen that considerable variations in signal level
may be achieved simply by altering the geometry
105 of the KD barrier, e.g. the signal will be higher the
higher the effective diffusion cross sectional area
and the shorter the effective diffusion path length.
Examples will now be given of the details of the
KD barrier used in various of the constructions
110 described above.

EXAMPLE 1
For use in the construction of Figure 1, a KD
barrier was made by stretching a 0.24 mm PTFE
tape supplied by W. L. Gore and Associates (UK)
115 Limited, described as clear, unsintered,
unstretched tape and having a porosity of about
15%. The tape was stretched laterally to six times
its original width and a piece of the stretched tape
was used for the barrier, having the following
120 dimensions, cross section 1.5 mm × 0.32 mm,
length (in the stretched direction) 3 mm. This gav
an oxygen sensor having a signal (in ambi nt air)
of 47 mV when loaded with a resistor of 47 ohms
(1 mA).

125 EXAMPLE II
For use with the constructions of either Figures
2 or 3, PTFE powder made from GP 1 dispersion
manufactured by Imperial Chemical Industri s

Limited was pressed into an opening 14 of
diameter 1.5 mm and length 1.3 mm in a top cap
15. It was then consolidated at a pressure of
about 2000 psi and the resultant oxygen sensor
5 gave a signal in ambient air of 40 mV when loaded
with a resistance of 47 ohms (0.85 mA).

EXAMPLE III
This was a modification of Example II in that the
opening 14 was slightly tapered and had a
10 minimum diameter of 0.5 mm and a length of
2.5 mm. It was filled with the same PTFE powder
as in Example II and this was consolidated at
5000 psi. The resultant oxygen sensor gave a
signal in ambient air of 9.0 mV when loaded with
15 a 47 ohms resistor.

EXAMPLE IV
For use with a top cap as illustrated in Figure 5,
a piece of "Tygaflor" R 12.8 gauge 7T PTFE tape
was used, as received, in the form of a disc of
20 6 mm diameter in conjunction with a top cap 15
having an opening 14 of 1.3 mm diameter and the
resultant oxygen sensor gave a signal of 45 mV in
ambient air when loaded with 47 ohms.
The KD sensors quoted in these Examples and
25 other sensors made in a similar fashion all had the
characteristics, which as described earlier,
distinguish them uniquely from SM or GP barrier
sensors. For example,
(1) Temperature co-efficient. Low negative co-
30 efficient close to —0.17% per °C (cf SM sensors,
high positive of the order of 2% to 3% per °C. GP
barrier sensors, positive around +0.17% per °C).
(2) Pressure co-efficient. At a given percentage
oxygen the signal from the KD sensors is
35 substantially proportional to the total pressure
indicating that they are responding directly to
partial pressure. (GP barrier sensors give a steady
state signal substantially independent of total
pressure, indicating that they are responding to %
40 oxygen rather than partial pressure).
It will be readily appreciated that these differing
characteristics can lead to specific advantages for
specific applications. If a substantially zero
temperature co-efficient is required, the
45 construction of Figure 6 may be used in
accordance with the following Example.

EXAMPLE V
For this purpose a KD barrier was composed of
two thicknesses of the same PTFE tape as in
50 Example IV and has a diameter of 6 mm. When
used as the sole barrier, this gave a signal from the
resultant sensor of about 2 mA in ambient air. This
was used in series with a capillary shown as 27 in
Figure 6 having the following dimensions, length
55 2.5 mm and diameter 0.29 mm. A sensor using
this capillary alone as a GP barrier also gave a
signal f 2 mA in ambient air. When the two
barriers were us d in series, th r sultant sensor
gave a signal of 46 mV when loaded with a
60 47 ohms resistor. The temperature co-efficient
m asured between 0°C and 40°C was close to
zero (less than +0.01% of signal per °C) and the

pressure co-efficient in ambient air was half that
of a corresponding sensor using only a KD barrier.
65 This confirmed that the characteristics of a sensor
using a KD barrier in series with a GP barrier were
intermediate between the characteristics of
sensors using a KD barrier and a GP barrier
respectively.

70 CLAIMS
1. An electro-chemical sensor for the
measurement of concentrations of gas or vapour
in accordance with the limiting current principle
and comprising an electrolytic cell having a
75 sensing electrode, a counter electrode and an
intervening body of electrolyte, the sensor also
including a restriction to the rate of access of gas
or vapour to the sensing electrode in the form of a
porous diffusion barrier of which substantially all
80 the active pores are sufficiently small as to cause
diffusion through them to be in accordance with
the Knudsen principle.
2. A sensor according to claim 1, in which the
proportions of the barrier are such that the
85 minimum linear dimension across the part of the
barrier through which diffusion occurs measured
in the direction at right angles to the overall
direction of diffusion is less than twice the mean
linear dimension along the overall direction of
90 diffusion.
3. A sensor according to claim 1 or claim 2 in
which the barrier is constituted by a piece of
unsintered PTFE tape sealed across an opening in
a casing for the cell and covered by an impervious
95 cover formed with gas access openings at points
beyond the outer limits of the tape whereby
diffusion occurs radially inwardly through the tape
from the gas access openings in the cover to the
opening in the casing.
100 4. A sensor according to claim 1 or claim 2 in
which the barrier is constituted by a piece of
unsintered PTFE tape sealed within an opening in
a casing for the cell.
5. A sensor according to claim 4 in which the
105 tape has been stretched across its width
subsequent to manufacture and is arranged in the
opening in such a way that diffusion through the
barrier is along the direction of stretching.
6. A sensor according to claim 1 or claim 2 in
110 which the barrier is constituted by a body sealed
within an opening in a casing for the cell and
formed of compressed PTFE powder, the body
having been consolidated in situ in the opening
and thereby sealed in position.
115 7. A sensor according to any one of the
preceding claims and including a gas phase
diffusion barrier in series with th first barrier.
8. A sensor according to claim 7 in which th
gas phase diffusion barrier is constituted by a
120 capillary.
9. A sensor according to claim 7 or claim 8 in
which the characteristics of the two barriers are so
matched as to give substantially zero temperature
co-efficient.
125 10. A method of forming a diffusion barrier for a
sensor according to claim 6 in which a dispersion

of minute PTFE particles in water is dried, the
dispersing agent removed and the resultant pasty

mass consolidated by the application of pressure
of at least 1000 psi.